Solution Studies on the Triangular Incomplete Cuboidal Dimolybdenum–Tungsten Cluster Aqua Ion [Mo$_2$W(μ$_3$-O)(μ-O)$_3$(OH$_2$)$_9$]$^{4+}$; Crystal Structure of [NMe$_4$]$_5$[Mo$_2$W(μ$_3$-O)(μ-O)$_3$(NCS)$_9$]·C$_6$H$_5$Me†

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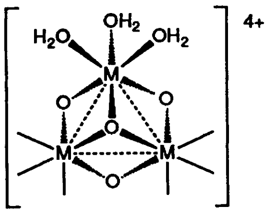
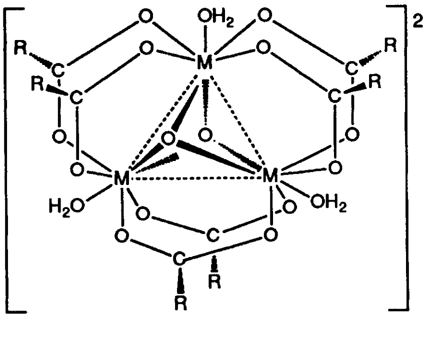
The synthesis and structural characterisation of the triangular incomplete cuboidal dimolybdenum–tungsten cluster aqua ion [Mo$_2$W(μ$_3$-O)(μ-O)$_3$(OH$_2$)$_9$]$^{4+}$ is reported. An X-ray crystallographic study of the derivative complex [NMe$_4$]$_5$[Mo$_2$W(μ$_3$-O)(μ-O)$_3$(NCS)$_9$]·C$_6$H$_5$Me shows positional disorder at the Mo and W atoms resulting in crystallographically identical metal sites ⅔ Mo and ⅓ W in character. Oxygen-17 and molybdenum-95 NMR measurements coupled with redox studies have verified the presence of the mixed cluster in solution. A kinetic study with regard to 1 : 1 NCS$^-$ substitution at the water ligands is supportive of reaction occurring at one of the two more labile and statistically identical and independent molybdenum sites promoted through a conjugate base form presumed to derive *via* deprotonation of a water ligand *trans* to the μ-O groups on the same molybdenum atom. Electronic effects on the redox and substitution behaviour at molybdenum arising from the presence of the remote tungsten atom have been detected.

The ready formation of triangular trinuclear cluster species is now well established as characterising the chemistry of both molybdenum and tungsten in oxidation state +4,[1–5] the triangular M$_3$ framework being rationalised as arising from the occupancy of three low-lying bonding molecular orbitals (MOs) (primarily M–M bonding in character) by the six d electrons. A number of different types of capping and bridging groups have been characterised in these systems ranging from oxide, sulfide and alkylidene (MeC^{3-}) (μ$_3$-capping) to oxide, sulfide, chloride and carboxylate (μ-bridging). Principal structure types I and II have been identified.[1]



I



II

Kinetic studies with regard to substitution at the terminal ligands, usually water, on a number of these species are in support of the existence of independent and, if C_{3v} or D_{3h} symmetry is relevant, identical metal sites within the cluster.[6–10] In the latter case this has meant an inability to assess remote-site electronic effects towards both redox and terminal ligand substitution properties at one given site. Sykes and co-workers,[11–13] in selectively replacing oxide ligands by sulfido at different positions in the incomplete cuboidal cluster type I (M = Mo), have perturbed the three-fold symmetry and detected kinetically distinct molybdenum sites with regard to replacement of water; the presence of μ-S groups accelerates the rate of substitution at a given molybdenum atom, all other things being equal, *versus* when μ-O groups are present. Thus concurrent NCS$^-$ substitution for water at non-equivalent molybdenum centres in the ion [Mo$_3$(μ$_3$-S)(μ-O)(μ-S)$_2$(OH$_2$)$_9$]$^{4+}$ was observed consistent with a statistical factor of two operative for the slow stage (substitution at the two molybdenum atoms carrying both μ-O and μ-S groups).[14]

Interest is growing in the alternative method of perturbing the three-fold symmetry in these clusters by the incorporation of different metal atoms and in particular those deriving from substitution of one or two molybdenum atoms by tungsten. A number of such mixed Mo/W derivatives have been reported, the earliest being the isopropoxide complexes [Mo$_2$W(μ$_3$-CMe)(μ-OPr^i)$_3$(OPr^i)$_6$] and [Mo$_2$W(μ$_3$-O)(μ$_3$-OPr^i)(μ-OPr^i)$_3$(OPr^i)$_6$] prepared by Chisholm *et al.*[15,16] Interestingly only the Mo$_2$W derivatives were reported. The complete series of Mo$_3$, Mo$_2$W, MoW$_2$ and W$_3$ derivatives has however been reported in the case of II[17] for X = O and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

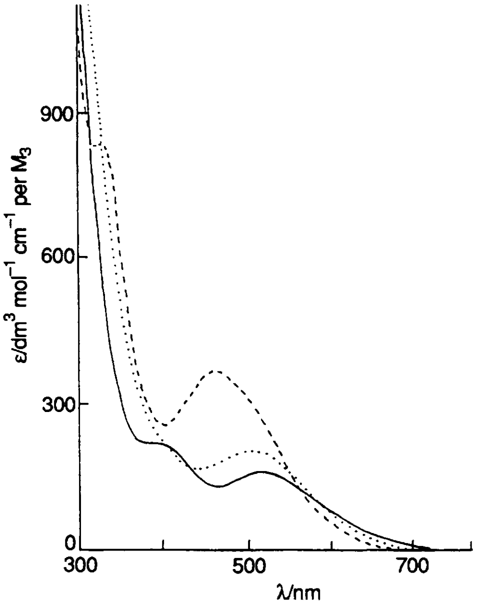

Fig. 1 Electronic spectra for solutions of $Mo_2WO_4{}^{4+}$(aq) (——), $Mo_3O_4{}^{4+}$(aq) (· · · ·) and $W_3O_4{}^{4+}$(aq) (– – – –) recorded in 2.0 mol dm^{-3} Hpts

R = Me. Here the complexes have been characterised by ^1H, ^{95}Mo and ^{183}W NMR in addition to UV/VIS spectrophotometry. Crystals of the above Mo/W derivatives are observed to be isomorphous with those of the Mo_3 and W_3 homometal species. Statistical disordering of the metal atom positions is also sometimes found to be a feature of these compounds. For $[M_3S_4(OH_2)_9]^{4+}$ (type **I**) structural characterisation of both the Mo_2W and MoW_2 derivatives was also recently reported[18] thus completing another series. Here the MoW_2 derivative was characterised as a minor product. The structure of the ion $[Mo_2W(\mu_3\text{-}S)(\mu\text{-}O)_2(\mu\text{-}S)(nta)_3]^{2-}$ (type **I**) (nta = nitrilotriacetate) has also been reported in a brief note.[19]

We report here the synthesis and characterisation of the triangular incomplete cuboidal aqua ion $[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ using ^{17}O and ^{95}Mo NMR spectroscopy in addition to electrochemical measurements and an X-ray structural characterisation of its NCS^- derivative. A kinetic study of 1 : 1 substitution of water by NCS^- at molybdenum is reported and the findings compared to those from corresponding studies on the homometal Mo_3 and W_3 cluster species. Electronic effects on the redox and substitution behaviour at molybdenum arising from the presence of the remote tungsten atom are considered. A preliminary account of this work has appeared.[20]

Experimental

Preparation of $[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$.—Samples of $K_2[MoCl_6]$ (0.9 g, 2.106 mmol, prepared *in situ* by reaction of $K_3[MoCl_6]$ with Br_2[21]) and $K_2[WCl_6]$[22] (0.5 g, 1.053 mmol) were thoroughly mixed and powdered in a 100 cm^3 Schlenk tube flushed with argon. Aqueous HCl (2.0 mol dm^{-3}, 50 cm^3) saturated with argon was then added and the mixture heated under argon on a steam-bath for 30 min. The resulting blue precipitate was subsequently filtered off and the purple-brown filtrate diluted to 0.5 mol dm^{-3} H^+ with deoxygenated water prior to loading onto a column (12 × 1 cm) of deoxygenated Dowex 50W X2 cation-exchange resin. Following washing of the column with water (250 cm^3) and then 0.5 mol dm^{-3} *p*-toluenesulfonic acid (Hpts) (Sigma), $[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$, as an air-sensitive purple-brown band, was eluted with 2.0 mol dm^{-3} Hpts. The Mo and W content of the solution was determined by flame atomic absorption spectrophotometry using samples of $[Mo_3O_4(OH_2)_9]^{4+}$ and $[W_3O_4(OH_2)_9]^{4+}$ ions as standards.* In this way the 2 : 1 stoichiometry of Mo to W was verified. The overall +4 oxidation state was verified by titration with Ce^{IV} using ferroin indicator. Typical solutions of $[Mo_2WO_4(OH_2)_9]^{4+}$ in 2.0 mol dm^{-3} Hpts gave the electronic spectrum shown in Fig. 1 possessing a peak maximum at 515 nm (ε 168 dm^3 mol^{-1} cm^{-1} per M_3) and a shoulder at ≈400 nm (ε ≈ 227 dm^3 mol^{-1} cm^{-1}). Similar features characterise the electronic spectrum of $[Mo_2WS_4(OH_2)_9]^{4+}$,[18] the bands here occurring at lower energy consistent with substitution of oxygen by sulfur. Attempts to make the corresponding $[MoW_2O_4(OH_2)_9]^{4+}$ ion by heating a 1 : 2 ratio of salts of Mo^{IV} to W^{IV} have so far failed, the resulting solutions being found to contain a mixture of $[Mo_2WO_4(OH_2)_9]^{4+}$ and $[W_3O_4(OH_2)_9]^{4+}$.

Preparation of ^{17}O-*Enriched Samples of* $[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$.—A slightly modified procedure was employed. Samples of $K_2[MoCl_6]$ (0.9 g, 2.106 mmol) and $K_2[WCl_6]$ (0.5 g, 1.053 mmol) were mixed and powdered as before. The mixture was then treated with concentrated HCl (11.0 mol dm^{-3}, 2 cm^3) followed by deoxygenated 12 atom% $H_2{}^{17}O$ (4 cm^3) (Yeda Co., Rehovot, Israel) and finally deoxygenated water (4 cm^3). The mixture was heated on the steam-bath for 30 min, filtered, and purified as above using Dowex X2 cation-exchange chromatography. Solutions of $[Mo_2WO_4(OH_2)_9]^{4+}$ concentrated enough for ^{17}O NMR measurements were prepared using a second small column (2 × 1 cm) of Dowex X2 resin with 4 mol dm^{-3} Hpts elution to give ≈1 cm^3 of solutions ≈0.02 mol dm^{-3} in complex. Further deoxygenated 12 atom% $H_2{}^{17}O$ (1 cm^3) containing Mn^{2+} ion (1 equivalent per average metal, see below) was added and the resulting mixture sealed within a standard 10 mm tube.

Other Reagents.—Lithium trifluoromethanesulfonate Li(tfms)·xH₂O and Mn(tfms)₂·yH₂O were prepared by neutralisation of solutions of the acid (Fluka) with the respective carbonate and recrystallised twice from water–ethanol. Values of x and y were determined by exchange of aqueous solutions onto an Amberlite IR 120H cation column (H^+ form) and titration of the resulting acid with standard NaOH.

NMR Measurements.—These were performed on a Bruker MSL-500 spectrometer using either a spinning 10 mm tube in a standard high-resolution probe (^{17}O) or a static 10 mm diameter sealed glass boat placed within a solenoid probe (^{95}Mo). Oxygen-17 NMR spectra were obtained at 67.796 MHz over a sweep range of 100 000 Hz following transformation of typically 50 000–130 000 accumulations (90° pulse width 27 μs) using 100 Hz line-broadening. Spline functions were applied to correct for the rolling baseline. Mn^{2+}, added as $Mn(tfms)_2$, was present in order to relax efficiently the ^{17}O resonance line of bulk water thus enabling monitoring of the region ± 50 ppm from bulk water referenced as δ 0. Molybdenum-95 NMR spectra were obtained at 32.596 MHz and at 40 °C over a sweep range of 500 000 Hz following transformation of ≈50 000 accumulations (90° pulse 18 μs) using 500 data points. The spectra were referenced to that from a 1.0 mol dm^{-3} solution of Na_2MoO_4.

Preparation of Derivative Complexes.—(*i*) $[NMe_4]_5[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(NCS)_9]$. A sample of $[Mo_2WO_4(OH_2)_9]^{4+}$ was

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* Atomic absorption spectroscopy was carried out using a fuel-enriched flame on a Pye-Unicam SP9 spectrometer. Settings were as follows: wavelength 313.3 nm (Mo), 255.1 nm (W); fuel flow rate N_2O 5.5 dm^3 min^{-1}, C_2H_2 4.8 dm^3 min^{-1} (Mo), N_2O 6.5 dm^3 min^{-1}, C_2H_2 4.8 dm^3 min^{-1} (W). The $Mo_3O_4{}^{4+}$ and $W_3O_4{}^{4+}$ species were convenient standards since they provided the same oxidation state and solution matrix as that present in the Mo_2W mixed ion. Concentration ranges analysed were typically 0.05–0.5 mmol dm^{-3} (Mo) and 0.4–4.4 mmol dm^{-3} (W).

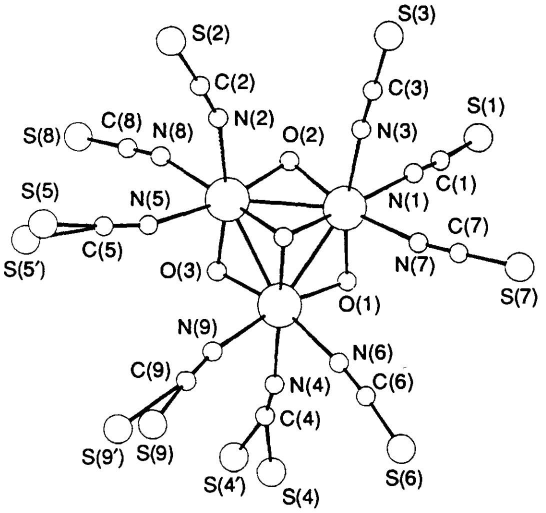


Fig. 2 The structure of the $[Mo_2WO_4(NCS)_9]^{5-}$ anion

loaded onto a small column (5 × 1 cm) of Dowex 50W X2 resin and washed with deoxygenated water (100 cm^3). A deoxygenated solution (2.0 mol dm^{-3}) of NaNCS was then passed down the column until smearing of the olive-green band on the column was observed. The column was left soaking in the NaNCS solution for 2 h and then eluted giving rise to a deep olive-green solution, treatment of which with a solution (0.5 mol dm^{-3}) of NMe_4Cl yielded a dark green microcrystalline precipitate (yield ≈ 80%) (Found: C, 26.15; H, 4.45; N, 14.80. Calc. for $C_{29}H_{60}Mo_2N_{14}O_4S_9W$: C, 26.15; H, 4.5; N, 14.70%). A crystal suitable for X-ray diffraction was grown by diffusion of toluene into a saturated solution of the complex in acetonitrile.

(*ii*) $Cs_{0.8}Na_{1.2}[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3\{NMe(CH_2CO_2)_2\}_3]\cdot 2H_2O$. This procedure was essentially identical to that reported by Wedd and co-workers[23] for the preparation of the corresponding Mo_3 compound. A short column (5 × 1 cm) of Dowex 50W X2 containing $[Mo_2WO_4(OH_2)_9]^{4+}$ was soaked overnight in deoxygenated 0.5 mol dm^{-3} sodium acetate–acetic acid (1 : 1) buffer and then eluted into a deoxygenated solution (0.5 mol dm^{-3}) of $Na_2[NMe(CH_2CO_2)_2]$ (Aldrich). Treatment of the resulting brown solution with CsCl eventually yielded pink microcrystals of the product following evaporation over silica gel (Found: C, 17.65; H, 2.45; N, 3.90. Calc. for $C_{15}H_{25}Cs_{0.8}Mo_2Na_{1.2}N_3O_{18}W$: C, 17.20; H, 2.40; N, 4.00%).

Crystallography.—X-Ray data were recorded on a crystal of approximate dimensions 0.12 × 0.125 × 0.28 mm, sealed under nitrogen in a thin-walled glass capillary, using a CAD4 diffractometer and graphite-monochromated Mo-Kα radiation following previously described procedures.[24]

Crystal data. $C_{29}H_{60}Mo_2N_{14}O_4S_9W\cdot C_7H_8$, $M = 1424.34$, triclinic, space group $P\bar{1}$, $a = 13.346(3)$, $b = 14.256(4)$, $c = 18.079(4)$ Å, $\alpha = 100.27(5)$, $\beta = 109.12(3)$, $\gamma = 84.88(5)°$, $U = 1734$ Å^3 (by least-squares refinement on 25 automatically centred reflections with $10 < \theta < 13°$), $Z = 2$, $D_c = 1.48$ g cm^{-3}. A total of 9734 reflections were measured to $\theta_{max} = 25°$, during which time a decay of *ca.* 36% occurred. A correction for this was applied during processing, followed by an empirical absorption correction based on ψ scans. After merging, 5873 unique reflections were obtained ($R_{int} = 0.05$) of which 5439 were observed [$F_o > 3\sigma(F_o)$].

The heavy-atom triangle was located by direct methods and the remaining atoms, some with difficulty, from successive refinement/difference-map cycles. The refinement showed quite conclusively that the three atom sites were equivalent, and reasonable thermal parameters were obtained when they were assigned scattering factors for [$\frac{2}{3}$Mo + $\frac{1}{3}$W]. The final stages of structure development and refinement were complicated by disorder or high thermal motion in a number of regions. Three of the cluster-bonded NCS^- ligands showed split sulfur sites [S(4,4′), S(5,5′), S(9,9′)] and these were assigned suitable fractional occupancies. Three of the five NMe_4 groups were fully identified, although all component atoms showed high *U* values. One cation showed disorder over at least two orientations and one could not be fully identified. One molecule of toluene of solvation was recognised however. In the last cycle only the non-disordered atoms of the cluster were refined anisotropically whereas all other atoms were refined isotropically. As a result of these features the *R* value obtained is higher than usual at $R = 0.085$ for 171 parameters. A unit weighting scheme gave the most satisfactory agreement analyses. The maximum shift/error in the final cycle refinement was 0.095 for U_{22} of a methylammonium carbon. The largest excursions in the final difference map were +1.4 and −1.0 e Å^{-3}. Fractional atomic coordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Kinetic Studies of 1 : 1 *NCS Substitution.*—Here stock solutions of $Mo_2WO_4^{4+}$ prepared by elution from the Dowex column with 2.0 mol dm^{-3} trifluoromethanesulphonic acid (Htfms) (Fluka) were employed. Runs were followed on the conventional time-scale at 325 nm (largest absorbance change) in 1 cm^3 quartz cells using a Perkin Elmer Lambda 5G spectrophotometer fitted with electronic thermostatting (±0.1 °C) and auto-cell change facilities. Solutions were manipulated under air-free conditions using nylon syringes, stainless steel needles, rubber septum caps and narrow gauge Teflon tubing as described previously.[25] The variation in [NCS^-] (0.0012–0.0035 mol dm^{-3}) maintained a pseudo-first-order excess (10-fold) over [Mo_2W] (typically 4.0 × 10^{-5} mol dm^{-3}). Runs were followed at 25 °C over the range [H^+] 0.3–1.95 mol dm^{-3}. For [H^+] = 1.95 mol dm^{-3} several runs were conducted with [Mo_2W] in 10-fold excess over [NCS^-]. The ionic strength was maintained at 2.0 mol dm^{-3} using Li(tfms). Values of k_{obs} were found from the slopes of $\ln(A_\infty - A_t)$ *vs.* *t* plots. In some cases A_∞ values were estimated using the method of Swinbourne.[26] Typical plots were linear to ⩾3 half-lives and appropriate for 1 : 1 complexation of NCS^- to $[Mo_2WO_4(OH_2)_9]^{4+}$. For [NCS^-] > 3.5 × 10^{-3} mol dm^{-3} biphasic plots, consistent with substitution of a second NCS^- ligand, were observed.

Electrochemistry.—Cyclic voltammograms were conducted on typically 5 mmol dm^{-3} deoxygenated solutions in 2.0 mol dm^{-3} Hpts employing a standard three-electrode cell design consisting of a mercury-cup working electrode, platinum-wire secondary electrode and saturated calomel reference electrode. The Hg drop area was typically 0.03–0.05 cm^2. The potential at the working electrode was controlled using a Princeton Applied Research model 170 electrochemical system with built in signal generator and Houston X-Y plotter. Typical scan rates were 0.1 V s^{-1}.

Results and Discussion

Structure of $[NMe_4]_5[Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3(NCS)_9]\cdot C_6H_5Me$.—A diagram of the anion is shown in Fig. 2, and includes representation of the disorder in three of the thiocyanate groups. Bond lengths and angles in the anion are given in Table 2. The average M–M bond length (2.521 Å) was found to lie almost exactly between those typically observed for the homometal Mo_3 (2.49 Å)[23,27–29] and W_3 (2.53 Å)[30] clusters of type **I** (X = O) showing a distinct trend in expansion of the M–M bond length as Mo is replaced by W. This is however in contrast to the bicapped clusters represented by $[M_3O(OR)_{10}]$[15,16] and $[M_3(\mu_3\text{-}O)_2(\mu\text{-}RCO_2)_6(OH_2)_3]^{2+}$[17]

Table 1 Fractional atomic coordinates (× 10^4) for $[NMe_4]_5[M_3O_4(NCS)_9]\cdot C_6H_5Me$ (M_3 = Mo_2W)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
M(1)	2 507(1)	2 336(1)	2 277(1)	C(12)	1 756(27)	2 729(26)	9 512(21)
M(2)	1 171(1)	1 863(1)	2 844(1)	C(13)	2 737(34)	3 897(30)	10 265(26)
M(3)	704(1)	3 174(1)	2 010(1)	C(14)	1 007(28)	4 234(25)	9 925(21)
O(1)	1 994(9)	1 133(8)	2 264(6)	N(20)	6 520(16)	1 251(14)	7 075(12)
O(2)	1 490(9)	2 605(8)	1 324(7)	C(21)	5 960(25)	2 157(22)	6 921(19)
O(3)	2(9)	2 056(8)	1 964(7)	C(22)	5 865(26)	442(24)	6 832(20)
O(4)	1 855(9)	3 135(7)	3 058(6)	C(23)	7 335(30)	1 280(26)	7 822(23)
N(1)	3 331(12)	1 583(12)	1 520(9)	C(24)	7 230(33)	1 140(30)	6 592(26)
C(1)	3 532(14)	1 079(15)	1 020(13)	N(30)	7 225(15)	5 220(14)	5 153(11)
S(1)	3 847(8)	416(8)	303(5)	C(31)	7 458(42)	4 677(38)	5 837(32)
N(2)	1 182(12)	4 566(11)	2 012(9)	C(32)	6 814(26)	4 512(24)	4 423(20)
C(2)	1 234(17)	5 363(17)	2 145(14)	C(33)	7 158(43)	6 099(38)	4 909(32)
S(2)	1 257(10)	6 502(6)	2 338(9)	C(34)	6 479(41)	5 257(37)	5 665(32)
N(3)	3 368(12)	3 540(11)	2 342(9)	C(35)	8 390(46)	5 033(43)	5 597(36)
C(3)	3 887(14)	4 169(18)	2 443(12)	C(36)	8 136(45)	5 676(41)	5 089(35)
S(3)	4 623(8)	5 079(7)	2 619(8)	C(37)	6 412(46)	5 899(42)	5 215(36)
N(4)	463(12)	543(11)	2 747(9)	N(40)	6 829(27)	2 136(24)	2 009(20)
C(4)	−28(18)	−94(15)	2 536(12)	C(41)	6 945(56)	1 505(55)	1 962(47)
N(5)	−269(12)	3 987(11)	2 610(10)	C(42)	6 046(48)	2 350(43)	2 168(37)
C(5)	−825(19)	4 512(17)	2 786(14)	C(43)	6 498(63)	2 442(59)	1 635(55)
C(6)	2 754(17)	1 365(20)	4 531(15)	C(44)	7 170(53)	2 034(51)	1 582(44)
S(6)	3 382(8)	1 066(14)	5 374(6)	N(50)	−67(49)	148(39)	−9(41)
N(7)	3 895(12)	2 113(11)	3 233(9)	C(51)	−426(52)	1 130(49)	−158(43)
C(7)	4 687(16)	2 063(14)	3 689(13)	C(52)	483(54)	864(50)	505(44)
S(7)	5 865(7)	1 979(9)	4 352(7)	C(53)	−1 066(63)	308(60)	−776(54)
N(8)	−545(12)	3 374(11)	964(9)	C(54)	1 160(52)	228(48)	94(42)
C(8)	−1 282(18)	3 242(14)	420(14)	C(55)	−117(65)	48(61)	−947(55)
S(8)	−2 354(8)	3 103(8)	−321(6)	C(101)	3 844(25)	3 212(22)	7 917(19)
N(9)	311(13)	2 429(11)	3 611(9)	C(102)	3 405(28)	2 383(27)	7 610(21)
S(4)	−433(15)	−1 197(13)	2 384(11)	C(103)	3 469(33)	1 505(31)	7 803(26)
S(4′)	−1 010(15)	−874(13)	2 152(11)	C(104)	4 172(30)	1 567(27)	8 516(24)
S(5)	−1 463(13)	5 454(11)	3 201(10)	C(105)	4 736(30)	2 327(29)	8 978(23)
S(5′)	−2 030(15)	5 007(14)	2 863(11)	C(106)	4 606(30)	3 239(28)	8 674(24)
N(6)	2 247(12)	1 531(11)	3 925(9)	C(107)	2 600(44)	2 378(39)	6 936(35)
C(9)	0(22)	2 651(19)	4 097(17)	C(112)	596(50)	−137(47)	4 621(41)
S(9)	−308(14)	3 064(12)	4 952(11)	C(113)	384(42)	380(38)	5 328(34)
S(9′)	−1 156(25)	2 758(21)	4 422(19)	C(114)	−1 134(44)	320(41)	4 224(35)
N(10)	1 803(16)	3 701(14)	9 636(12)	C(115)	−385(42)	−442(39)	5 368(34)
C(11)	1 833(22)	4 061(20)	8 924(17)				

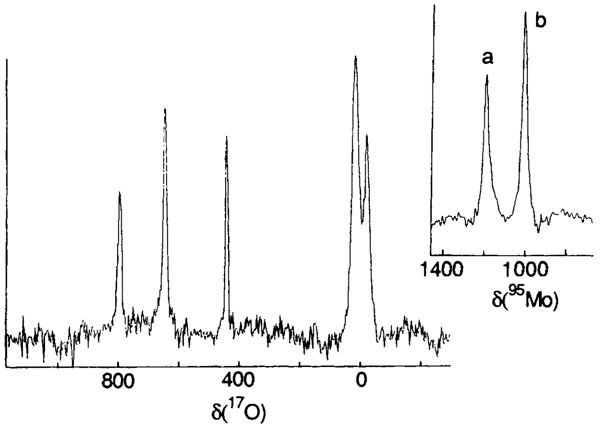
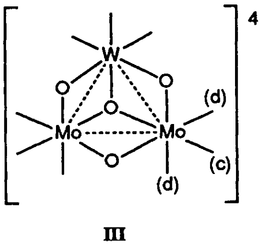


Fig. 3 67.796 MHz ^{17}O NMR spectrum of the $Mo_2WO_4^{4+}$(aq) cation (0.02 mol dm^{-3} in M_3) recorded in 4 mol dm^{-3} Hpts in the presence of Mn^{2+} (0.1 mol dm^{-3}), ^{17}O enrichment ≈6 atm%. [Inset: 32.596 MHz ^{95}Mo NMR spectrum of $Mo_2WO_4^{4+}$(aq) (0.02 mol dm^{-3}) (a) recorded in 4 mol dm^{-3} Hpts in the presence of $Mo_3O_4^{4+}$(aq) (b)]

(R = alkyl or aryl) which appear to show no discernable trend in bond lengths, the entire series of compounds being isomorphous.

Oxygen-17 *and Molybdenum*-95 NMR.—The ^{17}O NMR spectrum obtained from the fully enriched sample of $[Mo_2WO_4(OH_2)_9]^{4+}$ in Hpts solution is shown in Fig. 3 and assigned as follows: δ −22 and 16 (co-ordinated water), 442 (μ_3-O), 646 (Mo–O–W) and 815 (Mo–O–Mo). The co-ordinated water ligands relevant to the individual molybdenum and tungsten centres are not resolvable within the line-width, the overall appearance being of two peaks in a 1 : 2 ratio corresponding to the two types of water ligand, c (approximately *trans* to the capping μ_3-O group) and d (approximately *trans* to the bridging μ-O groups). The resonances at δ 442, 646 and 815 are in the expected 1 : 2 : 1 ratio consistent with their assignment within the $Mo_2W(\mu_3\text{-}O)(\mu\text{-}O)_3^{4+}$ core structure **III**. The resonance



III

at δ 815 is extremely close to that (δ 797) observed for the μ-oxygens of $Mo_3O_4^{4+}$ in support of its assignment to the μ-O group bridging the two molybdenum atoms. The resonances at δ 646 and 442 lie between those assigned respectively to the corresponding μ-O and μ_3-O groups in $[Mo_3O_4(OH_2)_9]^{4+}$ (δ 797 and 519)[31] and in $[W_3O_4(OH_2)_9]^{4+}$ (δ 560 and 313),[32] the position of the μ_3-O resonance, in being closer to that observed for $Mo_3O_4^{4+}$, reflecting bonding to two molybdenum

Table 2 Selected bond lengths (Å) and angles (°) for $[NMe_4]_5[M_3O_4(NCS)_9]\cdot C_6H_5Me$ ($M_3 = Mo_2W$)

M(2)–M(1)	2.519(5)	M(3)–M(1)	2.527(5)	N(4)–M(2)	2.135(19)	N(6)–M(2)	2.116(17)
O(1)–M(1)	1.897(14)	O(2)–M(1)	1.889(13)	N(9)–M(2)	2.091(21)	O(2)–M(3)	1.909(15)
O(4)–M(1)	2.025(14)	N(1)–M(1)	2.118(19)	O(3)–M(3)	1.896(14)	O(4)–M(3)	2.016(12)
N(3)–M(1)	2.115(19)	N(7)–M(1)	2.124(15)	N(2)–M(3)	2.136(19)	N(5)–M(3)	2.099(19)
M(3)–M(2)	2.517(5)	O(1)–M(2)	1.885(14)	N(8)–M(3)	2.116(16)	C(1)–N(1)	1.140(28)
O(3)–M(2)	1.869(12)	O(4)–M(2)	2.021(13)				
M(3)–M(1)–M(2)	59.9(2)	O(1)–M(1)–M(2)	48.0(4)	M(2)–M(3)–M(1)	59.9(2)	O(2)–M(3)–M(1)	48.0(3)
O(1)–M(1)–M(3)	94.4(4)	O(2)–M(1)–M(2)	95.0(5)	O(2)–M(3)–M(2)	94.5(5)	O(3)–M(3)–M(1)	93.6(4)
O(2)–M(1)–M(3)	48.6(4)	O(2)–M(1)–O(1)	96.8(6)	O(3)–M(3)–M(2)	47.6(3)	O(3)–M(3)–O(2)	96.1(6)
O(4)–M(1)–M(2)	51.4(4)	O(4)–M(1)–M(3)	51.2(4)	O(4)–M(3)–M(1)	51.4(4)	O(4)–M(3)–M(2)	51.5(4)
O(4)–M(1)–O(1)	98.7(6)	O(4)–M(1)–O(2)	98.9(6)	O(4)–M(3)–O(2)	98.5(6)	O(4)–M(3)–O(3)	98.4(6)
N(1)–M(1)–M(2)	133.5(6)	N(1)–M(1)–M(3)	132.7(4)	N(2)–M(3)–M(1)	98.0(5)	N(2)–M(3)–M(2)	140.5(4)
N(1)–M(1)–O(1)	85.7(7)	N(1)–M(1)–O(2)	84.3(6)	N(2)–M(3)–O(2)	91.5(7)	N(2)–M(3)–O(3)	168.5(5)
N(1)–M(1)–O(4)	174.1(5)	N(3)–M(1)–M(2)	139.4(5)	N(2)–M(3)–O(4)	89.0(6)	N(5)–M(3)–M(1)	140.9(4)
N(3)–M(1)–M(3)	96.7(5)	N(3)–M(1)–O(1)	168.9(5)	N(5)–M(3)–M(2)	96.4(6)	N(5)–M(3)–O(2)	168.9(6)
N(3)–M(1)–O(2)	90.8(6)	N(3)–M(1)–O(4)	88.0(7)	N(5)–M(3)–O(3)	90.2(7)	N(5)–M(3)–O(4)	89.5(6)
N(3)–M(1)–N(1)	87.0(8)	N(7)–M(1)–M(2)	97.8(6)	N(5)–M(3)–N(2)	81.0(8)	N(8)–M(3)–M(1)	133.7(5)
N(7)–M(1)–M(3)	140.6(4)	N(7)–M(1)–O(1)	91.4(6)	N(8)–M(3)–M(2)	132.9(5)	N(8)–M(3)–O(2)	86.1(7)
N(7)–M(1)–O(2)	167.2(7)	N(7)–M(1)–O(4)	89.4(6)	N(8)–M(3)–O(3)	85.4(7)	N(8)–M(3)–O(4)	173.6(5)
N(7)–M(1)–N(1)	86.6(7)	N(7)–M(1)–N(3)	79.8(7)	N(8)–M(3)–N(2)	86.4(7)	N(8)–M(3)–N(5)	85.3(7)
M(3)–M(2)–M(1)	60.2(2)	O(1)–M(2)–M(1)	48.4(4)	M(2)–O(1)–M(1)	83.5(5)	M(3)–O(2)–M(1)	83.4(6)
O(1)–M(2)–M(3)	95.0(5)	O(3)–M(2)–M(1)	94.5(5)	M(3)–O(3)–M(2)	83.9(5)	M(2)–O(4)–M(1)	77.0(5)
O(3)–M(2)–M(3)	48.5(4)	O(3)–M(2)–O(1)	96.0(6)	M(3)–O(4)–M(1)	77.4(5)	M(3)–O(4)–M(2)	77.1(4)
O(4)–M(2)–M(1)	51.5(5)	O(4)–M(2)–M(3)	51.3(4)	C(1)–N(1)–M(1)	162.8(14)	S(1)–C(1)–N(1)	176.7(22)
O(4)–M(2)–O(1)	99.2(6)	O(4)–M(2)–O(3)	99.2(6)	C(2)–N(2)–M(3)	159.2(20)	S(2)–C(2)–N(2)	177.4(24)
N(4)–M(2)–M(1)	133.0(5)	N(4)–M(2)–M(3)	133.0(4)	C(3)–N(3)–M(1)	173.8(16)	S(3)–C(3)–N(3)	177.8(22)
N(4)–M(2)–O(1)	84.8(7)	N(4)–M(2)–O(3)	84.7(6)	C(4)–N(4)–M(2)	164.4(16)	S(4)–C(4)–N(4)	162.7(20)
N(4)–M(2)–O(4)	174.0(5)	N(6)–M(2)–M(1)	97.9(6)	S(4′)–C(4)–N(4)	166.5(20)	C(5)–N(5)–M(3)	164.5(20)
N(6)–M(2)–M(3)	140.8(4)	N(6)–M(2)–O(1)	91.3(7)	S(5)–C(5)–N(5)	167.8(20)	S(5′)–C(5)–N(5)	158.4(21)
N(6)–M(2)–O(3)	167.6(7)	N(6)–M(2)–O(4)	89.5(6)	C(6)–N(6)–M(2)	174.1(19)	S(6)–C(6)–N(6)	174.7(26)
N(6)–M(2)–N(4)	86.0(7)	N(9)–M(2)–M(1)	140.8(5)	C(7)–N(7)–M(1)	170.8(19)	S(7)–C(7)–N(7)	179.1(22)
N(9)–M(2)–M(3)	96.9(6)	N(9)–M(2)–O(1)	168.1(6)	C(8)–N(8)–M(3)	161.3(17)	S(8)–C(8)–N(8)	176.6(21)
N(9)–M(2)–O(3)	91.0(7)	N(9)–M(2)–O(4)	89.2(7)	C(9)–N(9)–M(2)	167.9(18)	S(9)–C(9)–N(9)	171.4(24)
N(9)–M(2)–N(4)	86.2(7)	N(9)–M(2)–N(6)	80.2(7)				

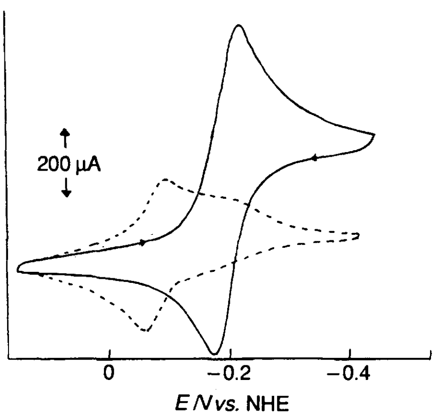


Fig. 4 Cyclic voltammograms for solutions (5×10^{-3} mol dm^{-3}) of $Mo_2WO_4^{4+}$(aq) (——) and $Mo_3O_4^{4+}$(aq) (· · ·) recorded at a mercury electrode at 0.1 V s^{-1} in 2.0 mol dm^{-3} Hpts

atoms. These findings suggest intermediate electronic properties for the oxygen atoms in the mixed-metal cluster in comparison to the homometal species. The ^{95}Mo NMR spectrum of $[Mo_2WO_4(OH_2)_9]^{4+}$ (inset Fig. 3) shows a single resonance at δ 1189 *vs.* that observed for $[Mo_3O_4(OH_2)_9]^{4+}$ (δ 996) (shown for comparison). This parallels the corresponding findings with regard to other M_3 clusters wherein stepwise replacement of molybdenum atoms by tungsten gives rise to a steady downfield shift in the ^{95}Mo resonance.[33] A corresponding upfield shift in the ^{183}W resonance on replacing tungsten atoms by molybdenum has also been observed.[33] These findings have been rationalised as indicating a slightly lower formal oxidation state for the molybdenum atoms* and a slightly higher oxidation state for tungsten in the mixed-metal species. Such conclusions have been substantiated by measurement of the valence orbital binding energies for the two metals in a number of homometal and mixed-metal species.[35] Thus formal donation of negative charge from tungsten to molybdenum appears to take place in these oxo Mo–W species.

Electrochemistry.—A typical cyclic voltammogram for $[Mo_2WO_4(OH_2)_9]^{4+}$ in 2.0 mol dm^{-3} Hpts solution is shown in Fig. 4. A corresponding voltammogram obtained from $[Mo_3O_4(OH_2)_9]^{4+}$ under the same conditions is shown for comparison. The reversible wave at −0.2 V *vs.* normal hydrogen electron (NHE) is assigned to formation of the mixed-valence ion $Mo^{III}{}_2W^{IV}$. This has been substantiated in separate experiments by titration of $[Mo_2WO_4(OH_2)_9]^{4+}$ with 2 equivalents of Eu^{2+} ion ($E° = -0.36$ V *vs.* NHE) and by controlled-potential coulometry at −0.4 V wherein two electrons per Mo_2W unit are consumed. The (III)$_2$(IV) oxidation state was verified by titration against Ce^{IV}. Reduction occurring at the two molybdenum atoms was deduced on the basis of a similar potential, albeit ≈100 mV more negative, to that observed for formation of $Mo^{III}{}_2Mo^{IV}$ from $[Mo_3O_4(OH_2)_9]^{4+}$. The slightly more negative potential for reduction is however consistent with the results from NMR measurements in suggesting the presence of a slightly lower formal oxidation for molybdenum in the Mo_2W ion.† Further reduction to

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* It is known from ^{95}Mo NMR measurements that the chemical shift of di- and poly-nuclear clusters appears at lower field as the oxidation state becomes lower.[34]

† In the series of isopropoxide complexes a similar 100 mV more negative reduction potential was seen representing the Mo_2W complex *vs.* that for the Mo_3 species.[15,16]

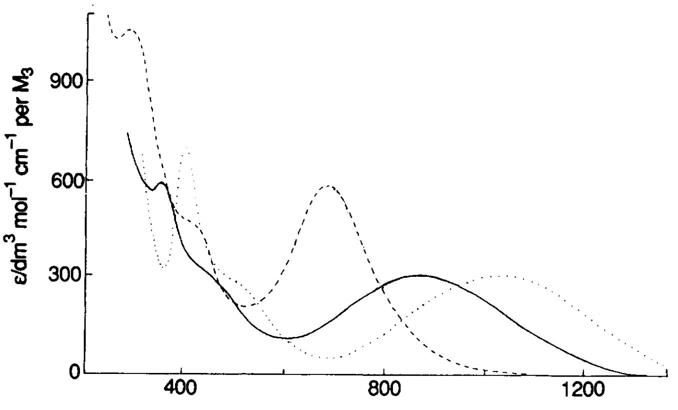
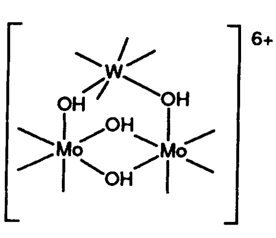


Fig. 5 Electronic spectra for solutions of the mixed-valence aqua ions $Mo^{III}_2W^{IV}$ (——); $Mo^{III}_2Mo^{IV}$ (· · · ·) and $W^{III}_2W^{IV}$ (– – – –) recorded in 2.0 mol dm^{-3} Hpts



IV

$Mo^{III}_2W^{III}$ requires the use of amalgamated zinc consistent with reduction now occurring at the tungsten atom. Remarkably the spectrum of $Mo^{III}_2W^{IV}$ shows similar overall features to those characteristic of the $Mo^{III}_2Mo^{IV}$[36] and $W^{III}_2W^{IV}$[30] aqua ions but lying exactly between them in energy (Fig. 5). Thus the band at 880 nm for $Mo^{III}_2W^{IV}$ is similarly assigned to a $Mo^{III} \longrightarrow W^{IV}$ charge-transfer transition. The structure of the $Mo^{III}_2W^{IV}$ ion may be represented by **IV** by analogy with studies conducted on the homo-molybdenum and -tungsten derivatives.[37]

These findings, taken with those from NMR measurements, indicate significant electronic interaction involving the metal centres in these clusters while at the same time maintaining their individual identity (*i.e.* class II mixed-valence character).

Kinetics of 1 : 1 NCS^- *Substitution on* $[Mo_2WO_4(OH_2)_9]^{4+}$.—With $[NCS^-]$ varied in pseudo-first-order excess over $[Mo_2W]$ a linear dependence of k_{obs} with $[NCS^-]$ was found passing through an intercept for all conditions of temperature and $[H^+]$ employed indicative of equilibration kinetics. Such behaviour parallels that correspondingly observed on the homometal $[Mo_3O_4(OH_2)_9]^{4+}$ (ref. 6) and $[W_3O_4(OH_2)_9]^{4+}$ (ref. 7) ions. Equilibration rate constants (k_{obs}, 25 °C) for runs carried out with $[NCS^-]$ in excess at five $[H^+]$ values are listed in Table 3 and illustrated in Fig. 6. For $[H^+] = 1.95$ mol dm^{-3} runs were also carried out with $[Mo_2W]$ in excess over $[NCS^-]$. Here identical rate constants were found to those obtained with $[NCS^-]/2$ in excess in support of statistical kinetics operating for the two identical and independent molybdenum atoms in the mixed cluster. The rate law [equation (1)] was thus relevant, k_f and k_b representing the

$$k_{obs} = k_f[Mo_2WO_4^{4+}] \text{ (or } [NCS^-]/2) + k_b \quad (1)$$

forward and back rate constants. At $[H^+] = 1.95$ mol dm^{-3} values of k_f for $[Mo_2WO_4(OH_2)_9]^{4+}$ were ≈60% those previously found for NCS^- substitution on $[Mo_3O_4(OH_2)_9]^{4+}$ in tfms$^-$ media[9] in support of substitution occurring at molybdenum. Both forward and back rate constants were found to increase on decreasing the $[H^+]$ suggesting that hydrolysis of $[Mo_2WO_4(OH_2)_9]^{4+}$ is kinetically important. A plot of k_f against $[H^+]^{-1}$ was sharply curved (Fig. 7) suggestive of a dependence of the type shown in equation (2) with K_{aMW} defined

$$k_f = \frac{k_0[H^+] + k_{OH}K_{aMW}}{[H^+] + K_{aMW}} \quad (2)$$

as the hydrolysis constant for formation of $[Mo_2WO_4(OH_2)_8(OH)]^{3+}$ and k_0 and k_{OH} defined as the rate constants for reaction of NCS^- with respectively $[Mo_2WO_4(OH_2)_9]^{4+}$ and $[Mo_2WO_4(OH_2)_8(OH)]^{3+}$. The data were fitted to (2) by use of an iterative non-linear least-squares treatment, the best fits being achieved on consideration of $k_0 = 0$. Consistent with this a linear plot of k_f^{-1} against $[H^+]$ was obtained (inset Fig. 7)

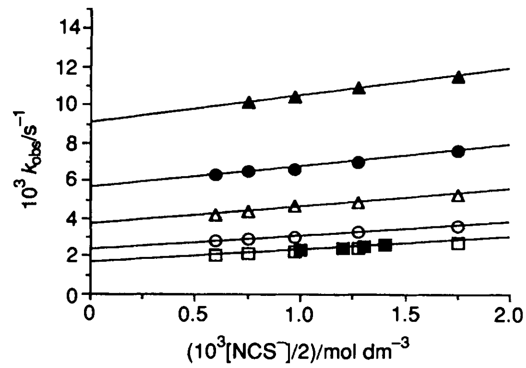


Fig. 6 Equilibration rate constants (25 °C) for 1 : 1 complexation of $Mo_2WO_4^{4+}$(aq) by NCS^- plotted linearly as a function of $[NCS^-]/2$ at 0.3 (▲), 0.6 (●), 1.0 (△), 1.5 (○) and 1.95 mol dm^{-3} (□); $I = 2.0$ mol dm^{-3} Li(tfms) [(■) runs conducted with $Mo_2WO_4^{4+}$(aq) in 10-fold excess]

Table 3 Equilibration rate constants (25 °C) obtained for the reaction of $Mo_2WO_4^{4+}$ with NCS^-, $I = 2.0$ mol dm^{-3} Li(tfms)

10^3 $[NCS^-]$/mol dm^{-3}	$[H^+]$/mol dm^{-3}	10^3 k_{obs}/s^{-1}
1.50	0.30	10.15
1.95		10.38
2.55		10.95
3.50		11.51
1.20	0.60	6.33
1.50		6.54
1.95		6.64
2.55		7.01
3.50		7.60
1.20	1.00	4.17
1.50		4.40
1.95		4.65
2.55		4.86
3.50		5.30
1.20	1.50	2.78
1.50		2.91
1.95		3.04
2.55		3.28
3.50		3.63
1.20	1.95	2.05
1.50		2.13
1.95		2.25
1.00*		2.37*
1.20*		2.47*
2.55		2.41
1.30*		2.57*
1.40*		2.65*
3.50		2.75

* Values obtained from runs with $Mo_2WO_4^{4+}$ in excess.

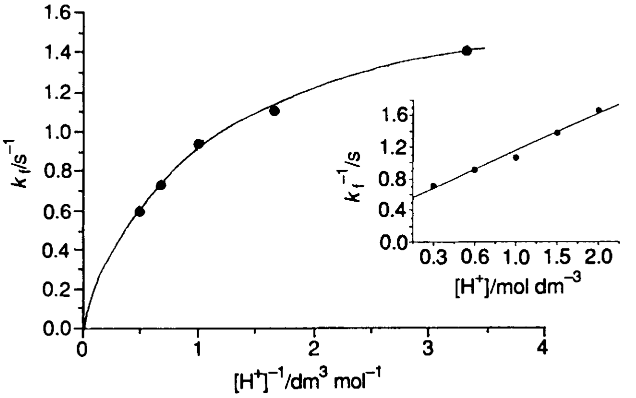


Fig. 7 Non-linear plot of k_f (NCS$^-$) *vs.* $[H^+]^{-1}$ (25 °C). (Inset: linear plot of k_f^{-1} *vs.* $[H^+]$)

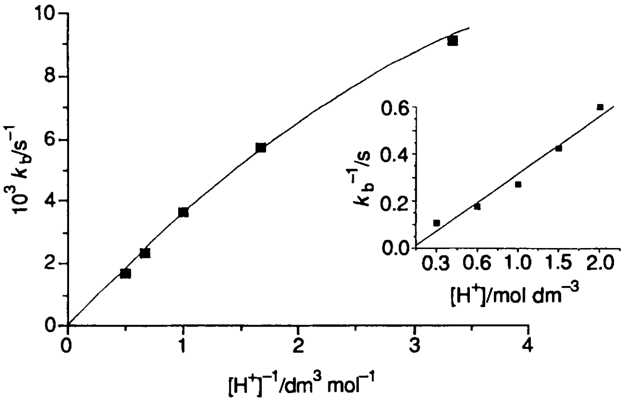


Fig. 8 Non-linear plot of k_b *vs.* $[H^+]^{-1}$ (25 °C). (Inset: linear plot of k_b^{-1} *vs.* $[H^+]$)

indicative of sole kinetic involvement of $Mo_2WO_4(OH)^{3+}$ in the substitution process. Values of k_{OH} and K_{aMW} found by iteration were respectively 1.80 ± 0.06 dm^3 mol^{-1} s^{-1} and 1.03 ± 0.08 mol dm^{-3} (25 °C). Finally using the K_{aMW} value so obtained a plot of $k_f([H^+] + K_{aMW})$ against $[H^+]$ gave a horizontal straight line indicative of little or no evidence for a pathway involving reaction of $[Mo_2WO_4(OH_2)_9]^{4+}$ with NCS$^-$. A corresponding plot of k_b *vs.* $[H^+]^{-1}$ (Fig. 8) was also curved with a subsequent plot of k_b^{-1} *vs.* $[H^+]$ (inset Fig. 8) found to be linear consistent with a similar expression [equation (3)] representing the back reaction where K_{aMWT} is the

$$k_b = \frac{k_{-OH}K_{aMWT}}{[H^+] + K_{aMWT}} \qquad (3)$$

hydrolysis constant for formation of $[Mo_2WO_4(OH_2)_7(OH)(NCS)]$. A non-linear least-squares fit to (3) gave values for k_{-OH} and K_{aMWT} respectively following iteration of 0.19 ± 0.1 s^{-1} and 0.02 ± 0.05 mol dm^{-3} (25 °C) respectively. Values for both k_f and k_b (25 °C) as a function of $[H^+]$ are shown in Table 4. The overall findings were thus consistent with the reaction scheme (4)–(6) (H_2O ligands excluded).

$$Mo_2WO_4^{4+} \xrightleftharpoons{K_{aMW}} Mo_2WO_4(OH)^{3+} + H^+ \qquad (4)$$

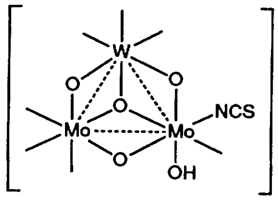
$$Mo_2WO_4(OH)^{3+} + NCS^- \xrightleftharpoons[k_{-OH}]{k_{OH}} Mo_2WO_4(OH)(NCS)^{2+} \qquad (5)$$

$$Mo_2WO_4(NCS)^{3+} \xrightleftharpoons{K_{aMWT}} Mo_2WO_4(OH)(NCS)^{2+} + H^+ \qquad (6)$$

Given that substitution is occurring on a water ligand at molybdenum it is presumed that the deprotonation responsible for generation of the kinetically relevant conjugate base also occurs at molybdenum, rapid proton transfer ensuring that both molybdenum atoms in the cluster remain statistically equivalent towards the incoming NCS$^-$ ligand. Reaction scheme (4)–(6) is identical to that established for NCS$^-$ substitution at water on $[Mo_3O_4(OH_2)_9]^{4+}$ and $[W_3O_4(OH_2)_9]^{4+}$. In the case of $[Mo_3O_4(OH_2)_9]^{4+}$ ^{17}O NMR studies have demonstrated that deprotonation occurs at one of the two H_2O ligands (d) approximately *trans* to the bridging μ-O groups,[27] the resulting conjugate base now believed to provide the dominant pathway for exchange at the d-H_2O ligands but not the c-H_2O ligands and responsible for the 10^5 × larger rate constant.[38] The kinetic importance of the conjugate base form coupled with the near identical rate constants observed for 1:1 NCS$^-$ and $HC_2O_4^-$ substitution and the apparent high co-ordination number at each metal strongly support a dissociative mechanism for water substitution at the d sites on these species. A comparison of the rate constant (k_f) for 1:1 reaction of NCS$^-$ on $[Mo_3O_4(OH_2)_9]^{4+}$ with the measured values for water exchange at the two sites[27] suggests a d-H_2O ligand as the likely site for substitution rather than the more inert c-H_2O (*trans* to the capping μ_3-O group). It would seem therefore reasonable to deduce that a deprotonated d-H_2O is involved in the present substitution of NCS$^-$ at an adjacent d-H_2O on molybdenum within $[Mo_2WO_4(OH_2)_8(OH)]^{3+}$ **V**.

Table 4 Forward and back rate constants (25 °C) for the reaction of $Mo_2WO_4^{4+}$ with NCS$^-$ as a function of $[H^+]$, I = 2.0 mol dm^{-3} Li(tfms)

$[H^+]$/mol dm^{-3}	k_f/dm^3 mol^{-1} s^{-1}	$10^3\ k_b$/s^{-1}
0.30	1.40	9.10
0.60	1.10	5.72
1.00	0.94	3.66
1.50	0.73	2.34
1.95	0.60	1.67



V

The large value of K_{aMW} for $[Mo_2WO_4(OH_2)_9]^{4+}$ (1.03 mol dm^{-3}) may be compared with similarly large values characterising the first hydrolysis constants for $[Mo_3O_4(OH_2)_9]^{4+}$ (0.4 mol dm^{-3})[6] and $[W_3O_4(OH_2)_9]^{4+}$ (0.2 mol dm^{-3})[7] (Table 5). The particularly large value observed here, if significant, will require to be substantiated by independent measurements. Interestingly for the ion $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ a higher K_{aM} (≈0.6 mol dm^{-3}), determined from the kinetics, was observed to correlate with a slower substitution rate for NCS$^-$ (factor of 10) *vs.* $[Mo_3O_4(OH_2)_9]^{4+}$.[39]

Comparison of rate constants (k_{OH}) for NCS$^-$ substitution on $[Mo_2WO_4(OH_2)_9]^{4+}$ with those observed for the homo Mo_3 and W_3 ions is unfortunately not directly possible since a full $[H^+]$ dependence has not been carried out on these latter species in tfms$^-$ media. However values for $[Mo_2WO_4(OH_2)_9]^{4+}$ and $[Mo_3O_4(OH_2)_9]^{4+}$ can be compared in tfms$^-$ at ≈2.0 mol dm^{-3} $[H^+]$ bearing in mind the presence of a larger amount of $[Mo_2WO_4(OH_2)_8(OH)]^{3+}$ due to the larger K_{aM}. The ≈60% lower rate constants observed for $[Mo_2WO_4(OH_2)_9]^{4+}$ (Table 5) would therefore appear to be significant

Table 5 Comparison of k_{OH} and K_{aM} values (25 °C) for 1:1 complexation of $M_3O_4(OH)^{3+}$(aq) ions with NCS^- (I = 2.0 mol dm^{-3})

M_3	k_{OH}/ dm^3 mol^{-1} s^{-1}	K_{aM}/ mol dm^{-3}	Medium	Ref.
Mo_3	4.8 ± 0.4	0.39 ± 0.05	2.0 mol dm^{-3} pts^-	6
	13.5[a]		2.0 mol dm^{-3} ClO_4^-	9
Mo_2W	1.80 ± 0.06[b]	1.03 ± 0.08	2.0 mol dm^{-3} $tfms^-$	This work
W_3	1.20 ± 0.17	0.20 ± 0.03	2.0 mol dm^{-3} ClO_4^-	7

[a] Calculated using a value for K_{aM} of 0.42 mol dm^{-3}. [b] No value of k_{OH} exists for reaction of NCS^- with $Mo_3O_4^{4+}$(aq) at I = 2.0 mol dm^{-3} $tfms^-$ for for comparison. In 2.0 mol dm^{-3} Htfms values of k_f (25 °C) can be compared as respectively 1.02 dm^3 mol^{-1} s^{-1} ($Mo_3O_4^{4+}$) and 0.6 dm^3 mol^{-1} s^{-1} ($Mo_2WO_4^{4+}$).

and could be a reflection of the greater electron density at molybdenum reducing its affinity for the incoming negatively charged NCS^- ligand.

The electronic spectra of the $M^{III}{}_2M^{IV}$ ions are certainly not suggestive of any particular tendency towards greater valence localisation in the Mo_2W species as opposed to the homometal analogues, the observations indeed showing that the properties of $[Mo_2WO_4(OH_2)_9]^{4+}$ lie essentially midway between those of the Mo_3 and W_3 species.

The detection of significant electron transfer occurring from tungsten to molybdenum, leading to an effective bond polarisation $Mo^{\delta-}$–$W^{\delta+}$, in mixed Mo/W trinuclear cluster ions containing bridging oxygen groups contrasts with the detection of no such corresponding electron transfer in the series of μ-sulfido cluster ions, $Mo_xW_{3-x}S_4^{4+}$. This has been ascribed[18] to an apparent buffering effect stemming from the softer nature of the bridging S atoms.

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